Transparent conducting aluminum-doped zinc oxide thin films for organic light-emitting devices

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Aluminum-doped zinc oxide (AZO) thin films ($\sim$3000 Å) with low electrical resistivity and high optical transparency have been grown by pulsed-laser deposition on glass substrates without a postdeposition anneal. Films were deposited at substrate temperatures ranging from room temperature to 400 °C in O_2 partial pressures ranging from 0.1 to 50 mTorr. For 3000-Å-thick AZO films grown at room temperature in an oxygen pressure of 5 mTorr, the electrical resistivity was 8.7×10^{-4} Ω cm and the average optical transmittance was 86% in the visible range (400–700 nm). For 3000-Å-thick AZO films deposited at 200 °C in 5 mTorr of oxygen, the resistivity was 3.8×10^{-4} Ω cm and the average optical transmittance in the visible range was 91%. AZO films grown at 200 °C were used as an anode contact for organic light-emitting diodes. The external quantum efficiency measured from these devices was about 0.3% at a current density of 100 A/m^2. © *2000 American Institute of Physics.* [S0003-6951(00)02603-6]

Recently, zinc oxide or impurity-doped zinc oxide films have been actively studied for use as a transparent conducting electrode material. Unlike the more commonly used indium tin oxide (ITO), zinc oxide (ZnO) is a nontoxic, inexpensive, and abundant material. It is chemically (and thermally) stable under hydrogen plasma processes that are commonly used for the production of solar cells.[1,2] ZnO is a II–VI *n*-type semiconductor with a band gap of about 3.3 eV at room temperature and a hexagonal wurtzite structure.[3] Doping of ZnO films with Al, Ga, and In has been reported to improve their stability as well as their electrical properties.[4–6] Among these doped ZnO films, Al-doped ZnO (AZO) films with about 0.5 at. % Al doping are reported to have low resistivities of $2-5 \times 10^{-4}$ Ω cm,[4,6–10] which is similar to what is observed for ITO films.[11–13] AZO films are also wide band gap semiconductors ($E_g = 3.4-3.9$ eV), which show good optical transmittance in the visible and near-infrared (IR) regions. Due to these unique properties, AZO films have been used as transparent conducting electrodes in solar cells.[1,2]

There are several deposition techniques which have been used to grow AZO thin films including chemical vapor deposition (CVD),[2,7] magnetron sputtering,[4,6,8] spray pyrolysis,[14,15] and pulsed-laser deposition (PLD).[9,10] In comparison with other techniques, PLD provides several advantages. The composition of the films grown by PLD is quite close to that of the target, even for multicomponent targets. PLD films crystallize at lower substrate temperatures due to the high kinetic energies (>1 eV) of the atoms and ionized species in the laser-produced plasma.[16] Also, the surface of the films grown by PLD can be very smooth.[11] ITO films, grown by PLD, have been used as the anode contact in or-

ganic light-emitting diodes (OLEDs),[11] however, there has been no report on the use of PLD to grow AZO anodes for OLEDs. In this letter, the electrical and optical properties of AZO films deposited by PLD on glass substrates and the performance characteristics of OLEDs with AZO anodes are reported.

Films were deposited on glass substrates using a KrF excimer laser (Lambda Physics LPX 305, 248 nm and pulse duration of 30 ns). Details of deposition are described elsewhere.[11–13] The laser was operated at a pulse rate of 10 Hz. The laser beam was focused through a 50 cm focal length lens onto a rotating target at a 45° angle of incidence. The energy density of the laser beam at the target surface was maintained at 2 J/cm^2. The target-substrate distance was 4.7 cm. The target was a 2-in.-diam by 0.25-in.-thick sintered oxide ceramic disk (98 wt % ZnO and 2 wt % Al_2O_3, 99.99% purity) supplied by Target Materials, Inc. The substrates were cleaned in an ultrasonic cleaner for 10 min with acetone and then methanol. The deposition chamber was initially evacuated to 1×10^{-5} Torr and during deposition, oxygen background gas was introduced into the chamber to maintain the desired pressure.

The film thickness was measured by a stylus profilometer (Tencor Alpha-Step 250). The film resistivity was determined from the sheet resistance measurement by a four-point probe technique. Hall mobility and carrier density measurements were made using the Van der Pauw method[17] at room temperature with a magnetic field strength of 5 kG. The optical transmission and reflectance measurements were made using a UV-visible-near-IR spectrophotometer (200–3200 nm) [Perkin-Elmer Lambda 9]. X-ray diffraction (XRD) [Rigaku rotating anode x-ray generator with Cu $K\alpha$ radiation] was used to characterize the crystal structure of the films. Ultraviolet photoelectron spectroscopy (UPS) was used to measure the work function of the films.

The electrical properties of the AZO films were mea-

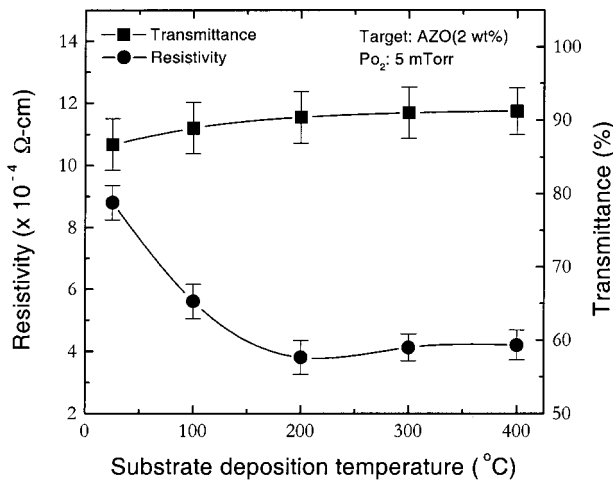[a)]Author to whom correspondence should be addressed; electronic mail: hskim@ccf.nrl.navy.mil

FIG. 1. Change in the electrical resistivity (ρ) and optical transmittance (T) as a function of substrate deposition temperature for the AZO films. Film thickness was about 3000 Å for all films. Oxygen pressure was kept in 5 mTorr during deposition. All transmittance values were determined as an average in the visible range from 400 to 700 nm.

FIG. 2. Variation of electrical resistivity (ρ) and optical transmittance (T) as a function of oxygen pressure for the AZO films grown at 25 and 200 °C. Film thickness was about 3000 Å for all films. All transmittance values were determined as an average in the visible range from 400 to 700 nm. ■ (ρ, 200 °C); ● (ρ, 25 °C); □ (T, 200 °C); ○ (T, 25 °C).

sured as a function of target composition, with varying Al_2O_3 content (0–10 wt %). It was observed that 2 wt % of Al_2O_3 in the target was the optimum composition to achieve the minimum film resistivity. Hence, the 2 wt % of Al_2O_3-doped ZnO target was used to deposit AZO films in this work. We have also performed the Hall effect measurements for the AZO films, all of which were observed to be *n*-type semiconductors. All the films deposited at room temperature were found to be amorphous while the films grown at temperatures greater than 100 °C were found to be crystalline and highly *c*-axis oriented with only the (002) and (004) reflections observed in the x-ray diffraction pattern.

The electrical and optical properties of AZO films were measured as a function of the substrate deposition temperature and oxygen deposition pressure. The substrate deposition temperature was found to have a significant effect on the electrical and optical properties of the AZO films. Figure 1 shows the variation of resistivity (ρ) and optical transmittance (T) as a function of substrate deposition temperature for the AZO films (~3000 Å). Deposition conditions other than substrate deposition temperature were maintained constant for each film. The resistivity of the AZO films decreases from 8.7×10^{-4} to 3.8×10^{-4} Ω cm as the substrate deposition temperature was increased from 25 °C to 200 °C. A slight increase in the resistivity is observed as the substrate deposition temperature is further increased from 200 to 400 °C. The initial decrease in resistivity with increase in deposition temperature can be attributed to an increase in the grain size of the AZO film from 120 to 180 Å with the increasing growth temperature, thus reducing the grain boundary scattering and increasing the conductivity. The slight increase in resistivity of the films grown at higher deposition temperature (300–400 °C) may be due to contamination of the alkali ions from glass substrates.[18–20] It is also observed that the optical transmittance increases slightly from 86% to 91% with an increase of the substrate temperature from 25 to 400 °C. This enhancement of optical transmittance is related to the improvement of the film crystallinity with increasing the substrate deposition temperature as
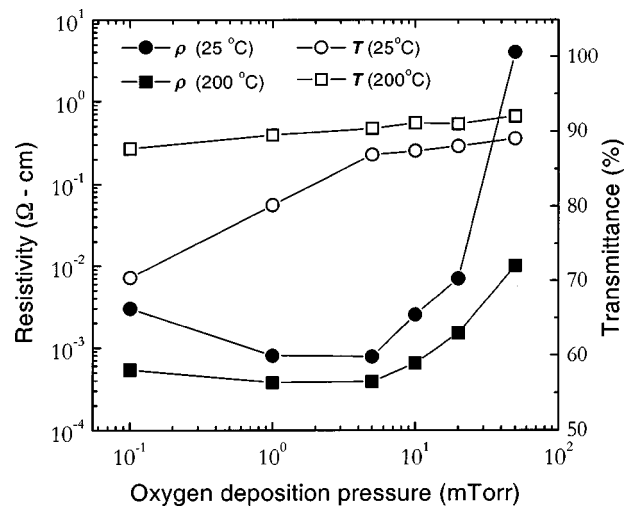
evidenced by a decrease in the width of the (002) XRD peak and an increase in the intensity of the (002) peak with increasing the substrate deposition temperature.

The oxygen deposition pressure was also found to affect the electrical and optical properties of the AZO films. Figure 2 shows the variation of electrical resistivity (ρ) and optical transmittance (T) as a function of oxygen deposition pressure for the AZO films (~3000 Å). The resistivity of the AZO films deposited at 25 °C is very sensitive to oxygen pressure. Low resistivity AZO films are obtained for films deposited at pressures between 1 and 5 mTorr of oxygen. However, the resistivity of the AZO films deposited at 200 °C is less dependent on the oxygen deposition pressure. The decrease in resistivity with a reduction of the oxygen deposition pressure from 50 to 5 mTorr can be explained by an increase in the number of oxygen vacancies in the AZO films. Decreasing the oxygen pressure from 50 to 5 mTorr increases the number of oxygen vacancies in the film and thus increases the carrier concentration in the film and decreases the film resistivity. However, this increase in carrier concentration also leads to a decrease in the optical transmittance due to an increase in free carrier absorption. Figure 2 shows this inverse relationship between the resistivity and transmittance of the AZO films. The optical transmittance increases with increasing oxygen pressure for the AZO films grown at both 25 and 200 °C. This increase in the optical transmittance is also related to the improvement of the film crystallinity with increasing the oxygen pressure since the width of the (002) XRD peak decreased and the intensity of the (002) peak increased with increasing oxygen pressure.

Figure 3 shows the current density–voltage–luminance ($J-V-L$) characteristics of an OLED with an AZO anode grown at 200 °C by PLD. The device structure used in this study, shown in the inset of Fig. 3(a), is made of a hole transport layer (HTL, ~500 Å) of N, N^*-diphenyl-N, N-bis (3-methylphenyl)1,1′-diphenyl-4,4′diamine (TPD), and an electron transport/emitting layer (ETL/EML, ~700 Å), of tris (8-hydroxyquinolinolato) aluminum (III) (Alq_3). The cathode contact deposited on top of the ETL is an alloy of
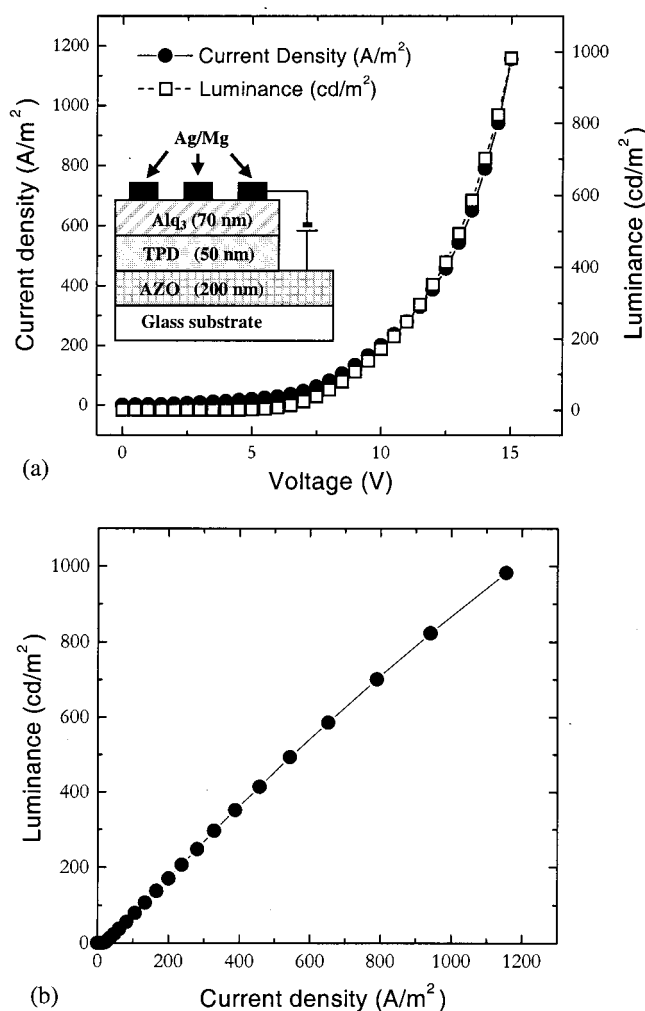
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FIG. 3. (a) Current density–voltage–luminance $(J-V-L)$ and (b) luminance–current density $(L-J)$ characteristics of a heterostructure device schematically represented in the inset of (a). An AZO film, grown by PLD at 200 °C in oxygen pressure of 5 mTorr, was used as an anode contact in this device.

Mg:Ag (ratio=12:1 and a thickness of 1500 Å). Details of fabrication of a similar device are described elsewhere.[21] The active area of the device is ~2 mm×2 mm. The J–V–L data were taken (in a dry N_2 atmosphere) using a Keithley current/voltage source and a luminance meter (Minolta LS-110). The J–V–L characteristics of the (AZO/TPD/Alq$_3$/MgAg) diode show a typical diode behavior, with the current and power output observed only in the forward bias. A voltage of ~8.4 V was measured at a current density of ~100 A/m^2. A luminance power efficiency of ~0.3 lm/W was observed at 100 cd/m^2. A luminance of ~1000 cd/m^2 was observed at 15 V and at a current density of ~1150 A/m^2. As seen in Fig. 3(b), the data for J and L superimpose quite well, in agreement with what is measured with a reference device fabricated with a commercially deposited ITO film (supplied by Planar America). However, the external quantum efficiency measured from the AZO device was $\eta_{ext.}\cong 0.3\%$ at ~100 A/m^2, which is lower than those measured ($\eta_{ext.}\cong 1.0\%$) from the reference (ITO) device. This low efficiency is due to the low work function (~4.0 eV) of the AZO in comparison to that of commercial ITO (4.5–4.8 eV). Similar work function value (4.23 eV)

was reported for the Ga-doped ZnO film prepared by metal-organic chemical vapor deposition (MOCVD).[22] Since the highest occupied molecular orbitals (HOMO) of the TPD lies ~5.5 eV below vacuum, there is a significant energy barrier ($\Delta E\approx 1.5$ eV) for hole injection from the AZO to the TPD layer.

In conclusion, AZO films have been deposited on glass substrates by PLD. At the optimized conditions for minimum resistivity and maximum transparency (200 °C and 5 mTorr of oxygen), the electrical resistivity of the AZO films was 3.8×10^{-4} Ω cm and the average optical transmittance in the visible range was 91%. The AZO films grown by PLD at 200 °C were used as an anode contact to fabricate OLEDs. The external quantum efficiency measured from these devices was about 0.3% at a current density of 100 A/cm^2. This low efficiency is due to the low work function (~4.0 eV) of the AZO in comparison to that of commercially sputter-deposited ITO (~4.5 eV). The low work function (~4.0 eV) of AZO makes it an attractive candidate for use as the cathode in OLEDs. Work is in progress to investigate AZO as a cathode material. AZO is still desirable for commercial production of OLED electrodes because it is an inexpensive and nontoxic material.

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